

Cation order and magnetic behaviour in mixed metal bismuth scheelite $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$

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The scheelites are a family of compounds with chemical formula ABO_4 , and a characteristic crystal structure consisting of AO_8 dodecahedra and BO_4 tetrahedra. This structure is flexible and can accommodate a large variety of cations with a range of atomic radii and valence combinations. Scheelite-type oxides, such as CaWO_4 , BiVO_4 and $\text{NaLa}(\text{MoO}_4)_2$ have been extensively studied due to their diverse range of physical and electronic properties [1]. In particular, Bi^{3+} containing molybdates have been found to be efficient photocatalysts due to the strong repulsive force of the $6s^2$ lone pair of Bi^{3+} , resulting in distortion of the BO_4 tetrahedra and alteration of the band gap [2, 3].

In 1974 $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$ (BFMO) was reported as the first scheelite-type compound containing trivalent cations on the tetrahedral sites [4]. Interestingly, two different polymorphs of BFMO can be isolated by varying the synthesis conditions [5]. The tetragonal scheelite-type polymorph, described by space group $I4_1/a$ with $a = 5.32106(13)$ Å and $c = 11.656(4)$ Å, can be prepared by a sol-gel route from aqueous solution of the constituent ionic species and has a disordered arrangement of the Fe and Mo cations. When heated above 500 °C, a 2:1 ordering of the Mo and Fe cations occurs, which lowers the symmetry to monoclinic ($C2/c$). The corresponding superstructure has a tripling of the a axis ($a = 16.9110(3)$ Å, $b = 11.6489(2)$ Å, $c = 5.25630(9)$ Å, $\beta = 107.1395(11)^\circ$). The two structures are illustrated in **Figure 1**.

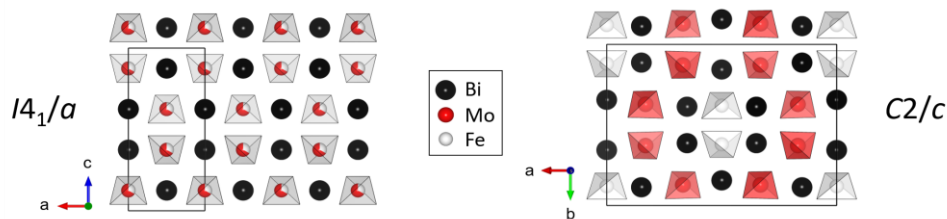


Figure 1: Disordered tetragonal $I4_1/a$ (left) and ordered monoclinic $C2/c$ (right) structures of $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$.

In the present study, both polymorphs of BFMO were synthesized and their structure and magnetic properties characterized using a combination of powder diffraction, microscopy and magnetometry techniques. *In situ* neutron powder diffraction (NPD) measurements of the structural evolution of disordered tetragonal BFMO with increasing temperature showed that no amorphization takes place prior to the formation of the ordered monoclinic phase. The lack of a structural break-down, despite the substantial cation movement required in such a transformation, suggests that a certain degree of local cation order exists in the “disordered” tetragonal phase, facilitating the direct conversion to the fully ordered monoclinic structure. Instead of the expected amorphization and recrystallization, the conversion takes place *via* a 1st order phase transition, with the tetragonal polymorph exhibiting negative thermal expansion prior to its conversion into the monoclinic structure. Zero-field-cooled/field-cooled and field-dependent magnetization curves of the monoclinic structure revealed the existence of a magnetic transition below 15 K. The long-range nature of the low-temperature magnetic structure in the monoclinic polymorph was verified by high-resolution NPD data, which revealed the emergence of an incommensurate magnetic structure. There is no evidence for long-range magnetic order in the tetragonal polymorph. This is, to the best of our knowledge, the first study of the phase transition mechanism and magnetic properties of this complex system and represents a milestone in the structural understanding and targeted design of Bi^{3+} containing molybdates as efficient photocatalysts.

[1] Brazdil, J. F. (2015). *Catalysis Science & Technology* **5**, 3452-3458.

[2] Feng, Y., Yan, X., Liu, C., Hong, Y., Zhu, L., Zhou, M. & Shi, W. (2015). *Appl Surf Sci* **353**, 87-94.

[3] Tokunaga, S., Kato, H. & Kudo, A. (2001). *Chem Mater* **13**, 4624-4628.

[4] Sleight, A. W. & Jeitschko, W. (1974). *Materials Research Bulletin* **9**, 951-954.

[5] Jeitschko, W., Sleight, A. W., McClellan, W. R. & Weiher, J. F. (1976). *Acta Crystallogr B* **32**, 1163-1170.

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